

Nonequilibrium Entropy

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Abstract

We consider an isolated system in an arbitrary state and provide a general formulation using first principles for an *additive* and *non-negative* statistical quantity $S_0(t)$ that is shown to reproduce the equilibrium thermodynamic entropy of the isolated system. We further show that $S_0(t)$ represents the nonequilibrium thermodynamic entropy $S_0(t)$ when the latter is a state function of nonequilibrium state variables; see text. We consider an isolated 1-d ideal gas and determine its non-equilibrium statistical entropy $S_0(t)$ as a function of the box size as the gas expands freely isoenergetically, and compare it with the equilibrium thermodynamic entropy S_{0eq} . We find that $S_0(t) \leq S_{0eq}$ in accordance with the second law, as expected. To understand how $S_0(t)$ is different from thermodynamic entropy of classical continuum models that is known to become *negative* under certain conditions, we calculate S_0 for a 1-d lattice model and discover that it can be related to the thermodynamic entropy of the continuum 1-d Tonks gas by taking the lattice spacing δ go to zero. However, $\Delta S_0 \neq \Delta S_0$ since δ is state-dependent. We discuss the semi-classical approximation of our entropy and show that the standard quantity $S_f(t)$ in the Boltzmann's H-theorem, see Eq. (3), does not directly correspond to the statistical entropy.

I. INTRODUCTION

Although the concept of entropy plays important roles in diverse fields ranging from classical thermodynamics of Clausius,¹⁻⁵ quantum mechanics and uncertainty,⁶⁻⁸ black holes,⁹ coding and computation,^{10,11} to information technology,^{12,13} it does not seem to have a standard definition. Here, we are interested in its application to nonequilibrium statistical thermodynamics. In classical thermodynamics, it is defined as a *thermodynamic* quantity with no association of any notion of a microstate and its probability, while modern approach to statistical thermodynamics, primarily due to Boltzmann and Gibbs, requires a probabilistic approach in terms of microstates. In this work, we are primarily interested in an isolated system Σ_0 . Quantities for the isolated system will carry a suffix 0; quantities without the suffix will refer to any body, which need not be isolated, such as a part Σ of Σ_0 ; see Fig. 1. The microstates for Σ_0 are determined by the set \mathbf{X}_0 of extensive observables (the energy E_0 , the volume V_0 , the number of particles N_0 , etc.) specifying the isolated system. While temporal evolution is not our primary interest in this work, we still need to remember the importance of temporal evolution in thermodynamics. We will say that two microstates belonging to the microstate subspace $\Gamma_0(\mathbf{X}_0)$ are "connected" if one evolves from the other after some time $\tau_0 < \infty$. Before this time, they will be treated as "disconnected." Let τ_{0max} denote the maximum τ_0 over all pairs of microstates. The space $\Gamma_0(\mathbf{X}_0)$ is *simply connected* for all times longer than τ_{0max} in that each microstate can evolve into another microstate $\in \Gamma_0(\mathbf{X}_0)$ in due time. For $t < \tau_{0max}$, the space $\Gamma_0(\mathbf{X}_0)$ will consist of *disjoint components*, an issue that neither Boltzmann nor Gibbs has considered to the best of our knowledge. But the issue, which we consider later in Sec. IIIB, becomes important in considering nonequilibrium states.

Boltzmann assumes *equal probability* of various microstates in the simply connected set $\Gamma_0(\mathbf{X}_0)$. Thus, τ_{0max} can be identified with the equilibration time

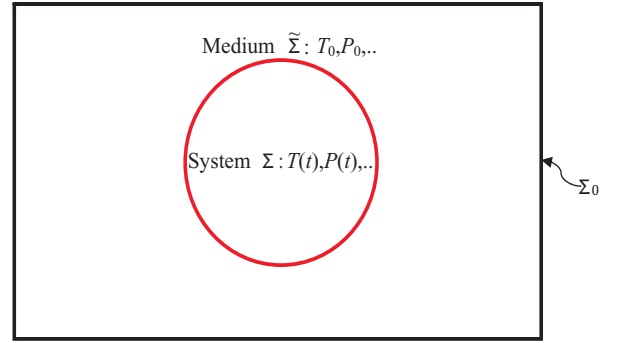


FIG. 1: Schematic representation of Σ , $\tilde{\Sigma}$ and Σ_0 . We assume that Σ and $\tilde{\Sigma}$ are homogeneous and in internal equilibrium, but not in equilibrium with each other. The internal fields $T(t), P(t), \dots$ of Σ and T_0, P_0, \dots of $\tilde{\Sigma}$ are not the same unless they are in equilibrium with each other. There will be viscous dissipation in Σ when not in equilibrium with $\tilde{\Sigma}$.

$\tau_{0eq}(\mathbf{X}_0)$ for Σ_0 . Under the equiprobable assumption, Boltzmann identifies the entropy in terms of the number of microstates^{5,14} $W_0(\mathbf{X}_0)$ in $\Gamma_0(\mathbf{X}_0)$:

$$S_{0B}(\mathbf{X}_0) \equiv \ln W_0(\mathbf{X}_0); \quad (1)$$

we will set the Boltzmann constant to be unity throughout the work so that the entropy will always be a *pure number*. The idea behind the above formula implicitly appears for the first time in a paper¹⁵ by Boltzmann, and then appears more or less in the above form later in his lectures¹⁶ where he introduces the combinatorial approach for the first time to statistical mechanics. The formula itself does not appear but is implied when he takes the logarithm of the number of combinations.^{16,17} (There is another formulation for entropy given by Boltzmann,^{15,16} which is also known as the Boltzmann entropy,¹⁸ that we will discuss later and that has a restricted validity; see Eq. (40).) Gibbs, also using the probabilistic approach, gives the following for-

mula for the entropy in a *canonical ensemble*:^{2,5}

$$S_G^{(c)} \equiv - \sum_{\alpha \in \Gamma_E} p_\alpha^{(c)} \ln p_\alpha^{(c)}; \quad \sum_{\alpha \in \Gamma_E} p_\alpha^{(c)} = 1 \quad (2)$$

where $p_\alpha^{(c)}$ is the canonical ensemble probability of the α th microstate of the system, and the sum is over all microstates corresponding to all possible energies E (with other elements in \mathbf{X} held fixed); their set is denoted by Γ_E in the above sum. The Gibbsian approach assumes an ensemble at a given instant, while the Boltzmann approach considers the evolution of a particular system in time; see for example a recent review.¹⁹ In equilibrium, both entropy expressions yield the same result. In quantum mechanics, this entropy is given by the von Neumann entropy formulation^{6,7} in terms of the density matrix ρ :

$$S_{vN} = -Tr(\rho \ln \rho).$$

The entropy formulation in the information theory^{12,13} has a form that appears to be similar in form to the above Gibbs entropy even though the temperature has no significance in the information theory. There is also another statistical formulation of entropy, heavily used in the literature, in terms of the phase space distribution function $f(x, t)$, which follows from Boltzmann's celebrated H-theorem:

$$S_f(t) = - \int f(x, t) \ln f(x, t) dx; \quad (3)$$

here, x denotes a point in the phase space. This quantity is not only not dimensionless but, as we will show later, is not the correct formulation in general; see Eq. (39a).

The classical thermodynamics entropy S_0 is oblivious to the microstates and their probabilities and deals with E_0, V_0, N_0 , etc. as the observables of the system. In equilibrium, the entropy S_0 is a state function, and can be expressed as a function of the observables. This functional dependence results in the Gibbs fundamental relation

$$dS_0 = \sum_p (\partial S_0 / \partial X_{0p}) dX_{0p} \quad (4)$$

in terms of the observables $\{X_{0p}\}$. For a lattice model, S_0 is non-negative in accordance with the Boltzmann definition of $S_{0B}(\mathbf{X}_0)$, but is known to become negative for a continuum model such as for an ideal gas. The latter observation implies that such continuum models are not realistic as they violate Nernst's postulate (the third law) and require *quantum mechanics* to ensure non-negativity of the entropy.⁵ Even the change ΔS_0 , the heat capacity, etc. do not satisfy thermodynamic consequences of Nernst's postulate.

By invoking Nernst's postulate (the equilibrium entropy vanishes at absolute zero), one can determine the equilibrium entropy everywhere *uniquely*. The consensus is that in equilibrium, the thermodynamic entropy is not different from the above statistical entropies due to Boltzmann and Gibbs. However, there is at present no consensus when the system is out of equilibrium. There

is also some doubt whether the nonequilibrium thermodynamic entropy has any meaning in classical thermodynamics. We will follow Clausius and take the view here that the thermodynamic entropy is a well-defined notion even for an irreversible process going on in a body for which Clausius¹ (p. 214) writes $TdS > d_e Q$ in terms of the exchange heat $d_e Q$ with the medium. The question that arises is whether the two statistical definitions can be applied to a body out of equilibrium. We find the answer to be affirmative. The next question that arises is the following: Do they always give the same results? We will show that under certain conditions, they give the same results. This is important as the literature is not very clear on this issue.²⁰⁻²³

For an isolated system, which we mostly consider here, we are not concerned with any thermostat or external working source. As a consequence, observables E_0, V_0, N_0 , etc. in \mathbf{X}_0 must remain constant even if the system is out of equilibrium. While this will simplify our discussion to some extent, it will also create a problem as we will discuss later. We discuss the concept of a nonequilibrium state, state variables and state functions in the next section. We introduce the statistical entropy formulation in Sec. III and show its equivalence with thermodynamic nonequilibrium entropy when the latter is a state function. In Sec. IV, we carry out an explicit quantum calculation of the nonequilibrium statistical entropy. In Sec. V, we consider a 1-d lattice model appropriate for Tonks gas in continuum so that the statistical lattice entropy can be calculated rigorously. We take the continuum limit and compare the resulting entropy with the continuum entropy of the Tonks gas and obtain an interesting result. We discuss the semi-classical approximation of the statistical entropy in Sec. VI and show that the formulation in Eq. (3) does not determine the entropy. A brief summary and discussion is presented in the final section.

II. THE SECOND LAW AND A NONEQUILIBRIUM STATE

A. Second Law

The second law states that the irreversible (denoted by a suffix i) entropy generated in any infinitesimal physical process going on in a body satisfies the inequality

$$d_i S \geq 0; \quad (5)$$

the equality occurs for a reversible process. For an isolated system, there is no exchange (denoted by a suffix e) entropy change $d_e S_0$ with the medium so that $dS_0 = d_e S_0 + d_i S_0$ in any arbitrary process. In an isolated system satisfies

$$dS_0 = d_i S_0 \geq 0. \quad (6)$$

The law refers to the *thermodynamic entropy*. It is not a state function in the conventional sense ($S_0(\mathbf{X}_0)$) if Σ_0

is not in equilibrium simply because as a state function $S_0(\mathbf{X}_0)$ must remain constant for constant \mathbf{X}_0 ; see below also.

As the thermodynamic entropy is not measurable except when the process is reversible, the second law remains useless as a computational tool. In particular, it says nothing about the rate at which the irreversible entropy increases. Therefore, it is useful to obtain a computational formulation of the entropy, the *statistical entropy*. This will be done in the next section. The onus is on us to demonstrate that the statistical entropy also satisfies this law if it is to represent the thermodynamic entropy. This by itself does not prove that the two are the same. It is not been possible to show that the statistical entropy is identical to the thermodynamic entropy in general. Here, we show their equivalence only when the nonequilibrium thermodynamic entropy is a *state function* of nonequilibrium state variables to be introduced below.

B. Concept of a Nonequilibrium State

For an isolated body in equilibrium, the entropy can be expressed as a function of its observables (variables that can be controlled by an observer), as is easily seen from the Gibbs fundamental relation in Eq. (4). The thermodynamic state, also known as the macrostate \mathcal{M}_0 , of a body in equilibrium remains the same unless it is disturbed. Therefore, we can identify the equilibrium state $\mathcal{M}_{0\text{eq}}$ of the body by its observables. Accordingly, its equilibrium entropy $S_0(\mathbf{X}_0)$ can be expressed as a function of its observables \mathbf{X}_0 . This is expressed by saying that the equilibrium entropy is a *state function* and \mathbf{X}_0 is the set of *state variables*.

The above conclusion is most certainly not valid for a body out of equilibrium, which we take to be isolated. If the body is not in equilibrium, its (macro)state $\mathcal{M}_0(t)$ will continuously change, which is reflected in its entropy change (increase) in time; this requires expressing its entropy as $S_0(\mathbf{X}_0, t)$ with an *explicit time-dependence*, since $\mathbf{X}_0 = \text{constant}$ for an isolated body. The change in the entropy and the macrostate must come from the variations of additional variables, distinct from the observables, that keep changing with time until the body comes to equilibrium as explained elsewhere.^{24,25} These variables cannot be controlled by the observer. Once the body has come to equilibrium, the entropy has no explicit time-dependence and becomes a state function. In this state, the entropy has its maximum possible value for given \mathbf{X}_0 . In other words, when the entropy becomes a state function, it achieves the maximum possible value for the given set of state variables, here given by \mathbf{X}_0 . This conclusion about the entropy will play an important role below.

We assume that there is a set ξ_0 of additional variables, known as the *internal variables* (sometimes also called hidden variables). We will refer to the variables in

\mathbf{X}_0 and ξ_0 as (*nonequilibrium*) *state variables* (see below for justification) and denote them collectively as \mathbf{Z}_0 in the following. From Theorem 4 presented elsewhere,²⁵ it follows that with a proper choice of the number of internal variables, the entropy can be written as $S_0(\mathbf{Z}_0(t))$ with no explicit t -dependence. The situation is now almost identical to that of an isolated body in equilibrium: The entropy is a function of $\mathbf{Z}_0(t)$ with no explicit time-dependence. This allows us to identify $\mathbf{Z}_0(t)$ as the set of nonequilibrium state variables. Thus, $\mathcal{M}_0(t)$ can be specified by $\mathbf{Z}_0(t)$ so that the entropy becomes a *state function*. This allows us to extend Eq. (4) to

$$dS_0 = \sum_p (\partial S_0 / \partial Z_{0p}) dZ_{0p} \quad (7)$$

in which the partial derivatives are related to the fields of the system:

$$(\partial S_0 / \partial E_0) = 1/T_0, (\partial S_0 / \partial V_0) = P_0/T_0, \dots \quad (8)$$

these fields will change in time unless the system has reached equilibrium.

As $\mathbf{Z}_0(t)$ changes in time, $\mathcal{M}_0(t)$ changes, but at each instant the (nonequilibrium) entropy as a state function, has a maximum possible value for given $\mathbf{Z}_0(t)$ even though $\mathcal{M}_0(t) \neq \mathcal{M}_{0\text{eq}}$. In our previous work,²⁴⁻²⁶ we have identified this particular state as an *internal equilibrium state*, but its physical significance as presented above was not discussed. For a state that is not in internal equilibrium, the entropy must retain an explicit time-dependence. In this case, the derivatives in Eq. (8) cannot be identified as state variables like, temperature, pressure, etc.

It may appear to a reader that the concept of entropy being a state function is very restrictive. This is not the case as this concept, although not recognized by several workers, is implicit in the literature where the relationship of the thermodynamic entropy with state variables is investigated. To appreciate this, we observe that the entropy of a body in internal equilibrium^{24,25} is given by the Boltzmann formula

$$S(\mathbf{Z}(t)) = \ln W(\mathbf{Z}(t)), \quad (9)$$

in terms of the number of microstates corresponding to $\mathbf{Z}(t)$. In classical nonequilibrium thermodynamics,²⁷ the entropy is always taken to be a state function. In the Edwards approach²⁸ for granular materials, all microstates are equally probable as is required for the above Boltzmann formula. Bouchbinder and Langer²⁹ assume that the nonequilibrium entropy is given by Eq. (9). Lebowitz²³ also takes the above formulation for his definition of the nonequilibrium entropy. As a matter of fact, we are not aware of any work dealing with entropy computation that does not assume the nonequilibrium entropy to be a state function. This does not, of course, mean that all states of a system are internal equilibrium states. For states that are not in internal equilibrium, the entropy is not a state function so that it will have an explicit time dependence. But, as shown elsewhere,²⁵

this can be avoided by enlarging the space of internal variables. The choice of how many internal variables are needed will depend on experimental time scales and cannot be answered in generality at present. We hope to come back to this issue in a future publication.

For a general body that is not isolated, the concept of its internal equilibrium state plays a very important role in that the body can come back to this state several times in a nonequilibrium process. In a cyclic nonequilibrium process, such a state can repeat itself in time after some cycle time τ_c so that all state variables and functions including the entropy repeat themselves:

$$\mathbf{Z}(t + \tau_c) = \mathbf{Z}(t), \mathcal{M}(t + \tau_c) = \mathcal{M}(t), S(t + \tau_c) = S(t).$$

This ensures $\Delta_c S \equiv S(t + \tau_c) - S(t) = 0$ in a cyclic process. All that is required for the cyclic process to occur is that the body must start and end in the same internal equilibrium state; however, during the remainder of the cycle, the body need not be in internal equilibrium.

III. GENERAL FORMULATION OF THE STATISTICAL ENTROPY

We provide a very general formulation of the statistical entropy, which will also demonstrate that the entropy is a *statistical average*. We consider a macrostate $\mathcal{M}_0(t) \equiv \mathcal{M}_0(\mathbf{Z}_0(t))$ of Σ_0 at a given instant t . In the following, we suppress t unless necessary. The macrostate $\mathcal{M}_0(\mathbf{Z}_0)$ refers to the set of microstates $\mathbf{m}_0 = \{m_{0\alpha}\}$ and their probabilities $\mathbf{p} = \{p_\alpha\}$. For the computation of combinatorics, the probabilities are handled in the following abstract way. We consider a large number $\mathcal{N}_0 = C_0 W_0(\mathbf{Z}_0)$ of independent *replicas* or *samples* of Σ_0 , with C_0 some large constant integer and $W_0(\mathbf{Z}_0)$ the number of distinct microstates $m_{0\alpha}$. The samples should be thought of as identically prepared experimental samples.¹⁹ Let $\Gamma_0(\mathbf{Z}_0)$ denote the sample space spanned by $m_{0\alpha}$.

A. Simply Connected Sample Space

1. An Isolated System

As $\Gamma_0(\mathbf{Z}_0) \subset \Gamma_0(\mathbf{X}_0)$, $\Gamma_0(\mathbf{Z}_0)$ is simply connected if $\Gamma_0(\mathbf{X}_0)$ is, which we assume in this section. Let $\mathcal{N}_{0\alpha}(t)$ denote the number of $m_{0\alpha}$ -samples (samples in the $m_{0\alpha}$ -microstate) so that

$$0 \leq p_\alpha(t) = \mathcal{N}_{0\alpha}(t)/\mathcal{N}_0 \leq 1; \quad \sum_{\alpha=1}^{W_0(\mathbf{Z}_0)} \mathcal{N}_{0\alpha}(t) = \mathcal{N}_0. \quad (10)$$

The above sample space is a generalization of the *ensemble* introduced by Gibbs, except that the latter is restricted to an equilibrium system, whereas our sample space refers to the system in any arbitrary state so that

p_α may be time-dependent. In the semi-classical approximation, see Sec. VI, one can similarly take the sample space to represent the classical phase space of Boltzmann. The (*sample* or *ensemble*) *average* of some quantity Q_0 over these samples is given by

$$\overline{Q_0} \equiv \sum_{\alpha=1}^{W_0(\mathbf{Z}_0)} p_\alpha(t) Q_{0\alpha}, \quad \sum_{\alpha=1}^{W_0(\mathbf{Z}_0)} p_\alpha(t) \equiv 1, \quad (11)$$

where $Q_{0\alpha}$ is the value of Q_0 in $m_{0\alpha}$.

The samples are, by definition, *independent* of each other so that there are no correlations among them. Because of this, we can treat the samples to be the outcomes of some random variable, the macrostate $\mathcal{M}_0(t)$. This independence property of the outcomes is crucial in the following, and does not imply that they are equiprobable. The number of ways \mathcal{W}_0 to arrange the \mathcal{N}_0 samples into $W_0(\mathbf{Z}_0)$ distinct microstates is

$$\mathcal{W}_0 \equiv \mathcal{N}_0! / \prod_{\alpha} \mathcal{N}_{0\alpha}(t)!. \quad (12)$$

Taking its natural log to obtain an *additive* quantity per sample

$$\mathcal{S}_0 \equiv \ln \mathcal{W}_0 / \mathcal{N}_0, \quad (13)$$

and using Stirling's approximation, we see easily that \mathcal{S}_0 , which we hope to identify later with the entropy $S_0(\mathbf{Z}_0(t))$ of the isolated system, can be written as the average of the negative of

$$\eta(t) \equiv \ln p(t),$$

what Gibbs² calls the *index of probability*:

$$\mathcal{S}_0(\mathbf{Z}_0(t), t) \equiv -\overline{\eta(t)} \equiv - \sum_{\alpha=1}^{W_0(\mathbf{Z}_0)} p_\alpha(t) \ln p_\alpha(t), \quad (14)$$

where we have also shown an explicit time-dependence for the reason that will become clear below. The above derivation is based on fundamental principles and does not require the system to be in equilibrium; therefore, it is always applicable. To the best of our knowledge, even though such an expression has been extensively used in the literature, it has been used *without* any derivation; one simply appeals to this form by invoking it as the information entropy; however, see Sec. VIII.

Because of its similarity in form with $S_G^{(c)}$ in Eq. (2), we will refer to $\mathcal{S}_0(\mathbf{Z}_0(t), t)$ as the Gibbs statistical entropy from now on. As the nonequilibrium thermodynamic entropy for a process in which the system is always in internal equilibrium can be determined by integrating the Gibbs fundamental relation in Eq. (7), we can compare it with the statistical entropy introduced above. However, such an integration is not possible for a process involving states that are arbitrary (not in internal equilibrium). Therefore, there is no meaning to compare $\mathcal{S}_0(\mathbf{Z}_0(t), t)$ with the corresponding thermodynamic entropy whose value cannot be determined. To identify $\mathcal{S}_0(\mathbf{Z}_0(t))$ with the nonequilibrium thermodynamic entropy requires the following additional steps:

- (1) It is necessary to establish that $\mathcal{S}_0(t)$ satisfies Eq. (6).
- (2) For an equilibrium canonical system, it is necessary to establish that $\mathcal{S}(t)$ is identical to the equilibrium thermodynamic entropy given by $S_G^{(c)}$.²
- (3) It is necessary to show that $\mathcal{S}_0(t)$ is identical to the nonequilibrium thermodynamic entropy of the system that is out of equilibrium but whose entropy is a state function.

There are several proofs available in the literature^{3,4,18,19,30} for (1). Therefore, we will not be concerned with (1) anymore. We will prove (2) and (3) in Sect. III A 2.

The maximum possible value of $\mathcal{S}_0(t)$ for given $\mathbf{Z}_0(t)$ occurs when $m_{0\alpha}$ are *equally probable*:

$$p_\alpha(t) \rightarrow p_{\alpha,\text{eq}} = 1/W_0(\mathbf{Z}_0), \quad \forall m_\alpha \in \Gamma_0(\mathbf{Z}_0).$$

In this case, the explicit time dependence in $\mathcal{S}_0(t)$ will *disappear* and we have

$$\mathcal{S}_{0,\text{max}}(\mathbf{Z}_0(t), t) = \mathcal{S}_0(\mathbf{Z}_0(t)) = \ln W_0(\mathbf{Z}_0(t)), \quad (15)$$

which is identical in form to the Boltzmann (thermodynamic) entropy in Eq. (1) for an isolated body in equilibrium, except that the current formulation has been extended to an isolated body out of equilibrium; see also Eq. (9). The only requirement is that all microstates in $\mathbf{m}_0 \equiv \mathbf{m}_0(\mathbf{Z}_0(t))$ are equally probable. The statistical entropy in this case becomes a state function.

Applying the above formulation to a macrostate characterized by a given \mathbf{X}_0 and consisting of microstates $\{\bar{m}_\alpha\}$, forming the set $\bar{\mathbf{m}}_0 \equiv \mathbf{m}_0(\mathbf{X}_0)$, with probabilities $\{\bar{p}_\alpha(t)\}$, we find that

$$\mathcal{S}_0(\mathbf{X}_0, t) \equiv - \sum_{\alpha=1}^{W_0(\mathbf{X}_0)} \bar{p}_\alpha(t) \ln \bar{p}_\alpha(t), \quad \sum_{\alpha=1}^{W_0(\mathbf{X}_0)} \bar{p}_\alpha(t) \equiv 1, \quad (16)$$

is the entropy of this macrostate, where $W_0(\mathbf{X}_0)$ is the number of distinct microstates \bar{m}_α . It should be obvious that

$$W_0(\mathbf{X}_0) \equiv \sum_{\xi_0(t)} W_0(\mathbf{Z}_0(t)).$$

Again, under the equiprobable assumption

$$\bar{p}_\alpha(t) \rightarrow \bar{p}_{\alpha,\text{eq}} = 1/W_0(\mathbf{X}_0), \quad \forall \bar{m}_\alpha \in \Gamma_0(\mathbf{X}_0),$$

$\Gamma_0(\mathbf{X}_0)$ denoting the space spanned by microstates $\{\bar{m}_\alpha\}$, the above entropy takes its maximum possible value

$$\mathcal{S}_{0,\text{max}}(\mathbf{X}_0, t) = \mathcal{S}_0(\mathbf{X}_0) = \ln W_0(\mathbf{X}_0), \quad (17)$$

which is identical in value to the Boltzmann (thermodynamic) entropy in Eq. (1) for an isolated body in equilibrium. The maximum value occurs at $t = \tau_{0\text{eq}}$. It is evident that

$$\mathcal{S}_0[\mathbf{Z}_0(t), t] \leq \mathcal{S}_0[\mathbf{Z}_0(t)] \leq \mathcal{S}_0(\mathbf{X}_0). \quad (18)$$

The anticipated identification of nonequilibrium thermodynamic entropy with \mathcal{S}_0 under some restrictions allows us to identify \mathcal{S}_0 as the *statistical entropy* formulation of the thermodynamic entropy. From now on, we will refer to the general entropy in Eq. (14) in terms of microstate probabilities as the *time-dependent Gibbs formulation* of the entropy or simply the *Gibbs entropy*, and will not make any distinction between the statistical and thermodynamic entropies. Accordingly, we will now use the regular symbol S_0 for \mathcal{S}_0 throughout the work, unless clarity is needed.

We will refer to $S_0(\mathbf{Z}_0(t))$ in terms of microstate number $W_0(\mathbf{Z}_0(t))$ in Eq. (15) as the *time-dependent Boltzmann formulation* of the entropy or simply the Boltzmann entropy,²³ whereas $S_0(\mathbf{X}_0)$ in Eq. (17) represents the equilibrium (Boltzmann) entropy. It is evident that the Gibbs formulation in Eqs. (14) and (16) supersedes the Boltzmann formulation in Eqs. (15) and (17), respectively, as the former contains the latter as a special limit. However, it should be also noted that there are competing views on which entropy is more general.^{22,23} We believe that the above derivation, being general, makes the Gibbs formulation more fundamental. The continuity of $S_0(\mathbf{Z}_0, t)$ follows directly from the continuity of $p_\alpha(t)$. The existence of the statistical entropy $S_0(\mathbf{Z}_0, t)$ follows from the observation that it is bounded above by $\ln W_0(\mathbf{Z}_0)$ and bounded below by 0, see Eq. (15).

It should be stressed that \mathcal{W} is not the number of microstates of the \mathcal{N} replicas; the latter is given by $[W_0(\mathbf{Z}_0)]^\mathcal{N}$. Thus, the entropy in Eq. (13) should not be confused with the Boltzmann entropy, which would be given by $\mathcal{N} \ln W_0(\mathbf{Z}_0)$. It should be mentioned at this point that Boltzmann uses the combinatorial argument to obtain the entropy of a gas, see Eq. (40), resulting in an expression similar to that of the Gibbs entropy in Eq. (2) except that the probabilities appearing in his formulation represents the probability of various discrete states of a particle, and should not be confused with the microstate probabilities used here; see Sec. VII. The approach of Boltzmann is *limited* to that of an ideal gas only and is not general as it neglects the correlations present due to the interactions between particles.^{18,23} On the other hand, our approach is valid for any system with any arbitrary interactions between particles as all microstates in the collection are *independent*.

2. System in a Medium and Quasi-independence

Using the above formulation of $S_0(\mathbf{Z}_0(t), t)$, we have determined²⁵ the statistical formulation of the entropy for a system Σ , which is a small but macroscopically large part of Σ_0 ; see Fig. 1. It is assumed that the system and the medium are *quasi-independent* so that $S_0(t)$ can be expressed as a sum of entropies $S(t)$ and $\tilde{S}(t)$ of the system and the medium, respectively:

$$S_0(t) = S(t) + \tilde{S}(t). \quad (19)$$

The two statistical entropies are given by an identical formulation

$$S(t) = -\sum_k p_k(t) \ln p_k(t), \quad \tilde{S}(t) = -\sum_k \tilde{p}_k(t) \ln \tilde{p}_k(t), \quad (20)$$

respectively. Here, m_k with probability p_k denotes a microstate of Σ and \tilde{m}_k with probability \tilde{p}_k that of the medium. In the derivation,²⁵ we have neither assumed the medium nor the system to be in internal equilibrium; only quasi-independence is assumed. The above formulation of statistical entropies will not remain valid if the two are not quasi-independent. The same will also be true of the thermodynamic entropies.

For the system to be in internal equilibrium, its statistical entropy $S(t)$ must be maximized under the constraints imposed by the medium. The constraints are on the average values of the state variables:

$$\mathbf{Z}(t) = \sum_k \mathbf{Z}_k p_k,$$

where \mathbf{Z}_k is the value of \mathbf{Z} in m_k . The condition for internal equilibrium is obtained by varying p_k without changing the microstates, i.e. \mathbf{Z}_k . Using the Lagrange multiplier technique, it is easy to see that the condition for this in terms of the Lagrange multipliers whose definitions are obvious is

$$-\ln p_k = \lambda_0 + \boldsymbol{\lambda} \cdot \mathbf{Z}_k; \quad (21)$$

the Lagrange multipliers are the same for all microstates and the scalar product is over the elements in the set \mathbf{Z}_k . It now follows that

$$S = \lambda_0 + \boldsymbol{\lambda} \cdot \mathbf{Z}(t), \quad (22)$$

using the same scalar product as above. It is now easy to identify the Lagrange multipliers by observing that

$$dS = \boldsymbol{\lambda} \cdot d\mathbf{Z}. \quad (23)$$

Comparing this relation with the Gibbs fundamental relation for the system, which follows from Eq. (7) when applied to the system, we find

$$\lambda_p \equiv (\partial S / \partial Z_p).$$

Accepting this identification now allows us to conclude that the statistical entropy $S(t)$ in Eq. (20) is no different than the nonequilibrium thermodynamic entropy of the same system in internal equilibrium but in a medium. A special case of such a system is the (equilibrium) canonical ensemble of Gibbs. This proves (2) mentioned in Sect. III A 1. In equilibrium, the Lagrange multipliers associated with the internal variables vanish and Eq. (23) reduce to

$$dS = \boldsymbol{\lambda} \cdot d\mathbf{X}. \quad (24)$$

The significance of λ_0 is quite obvious. In internal equilibrium, it is given by

$$\lambda_0 = S - (\partial S / \partial \mathbf{Z}) \cdot \mathbf{Z}(t).$$

Moreover, as the nonequilibrium entropy in internal equilibrium is a state function, it can in principle be measured or calculated by integrating Eq. (23). Therefore, its value can be compared with the statistical entropy. The above identification in Eq. (23) then proves (3).

If the thermodynamic entropy is not a state function, it cannot be measured or computed. Thus, while the statistical entropy can be computed in principle in all cases, as shown below explicitly, there is no way to compare its value with the thermodynamic entropy in all cases. Thus, no comment can be made about their relationship in general. We merely conjecture that as the two entropies are the same when the thermodynamic entropy is a state function, it is no different from its statistical analog even when it is not a state function.

B. Disjoint Sample Space (Component Confinement)

The consideration of dynamics resulting in the simple connectivity of the sample (or phase) space has played a pivotal role in developing the kinetic theory of gases,^{16,23} where the interest is at high temperatures.^{5,19,30,31} As dynamics is very fast here, it is well known that the ensemble entropy agrees with its temporal formulation. However, at low temperatures, where dynamics becomes sluggish as in a glass,^{32,33} the system can be *confined* into disjoint components.

Sample (or phase) space confinement at a phase transition such as a liquid-gas transition is well known in equilibrium statistical mechanics.^{5,19,30} It also occurs when the system undergoes symmetry breaking such as during magnetic transitions, crystallizations, etc. But confinement can also occur under nonequilibrium conditions, when the observational time scale τ_{obs} becomes shorter than the equilibration time τ_{eq} ,^{32,33} such as for glasses, whose behavior and properties have been extensively studied.

The issue has been recently considered by us,¹⁹ where only energy as an observable was considered. The discussion is easily extended to the present case when confinement occurs for whatever reasons into one of the thermodynamically significant number of disjoint components $\Gamma_{0\lambda}$, $\lambda = 1, 2, 3 \dots, \mathcal{C}$, each component corresponding to the same set \mathbf{Z}_0 or \mathbf{Z} (we suppress the dependence for simplicity), depending on whether the body is isolated or not. Such a situation arises, for example, in Ising magnets at the ferromagnetic transition, where the system is either confined to Γ_{0+} with positive magnetization or Γ_{0-} with negative magnetization. Even a weak external magnetic field $|H| \rightarrow 0$, that we can *control* as an observer, will allow the system to make a choice between the two parts of Γ_0 . It just happens that in this case $\mathcal{C} = 2$ and is thermodynamically insignificant.

The situation with glasses or other amorphous materials is very different.³² In the first place, Γ_0 is a union of *thermodynamically significant* number $\mathcal{C} \sim e^{cN}$, $c > 0$,

disjoint components. In the second place, there is no analog of a symmetry breaking field. Therefore, there is no way to prepare a sample in a given component $\Gamma_{0\lambda}$. Thus, the samples will be found in all different components. Taking into consideration disjointness of the components generalizes the number of configurations in Eq. (12) to

$$\mathcal{W}_0 \equiv \mathcal{N}_0! / \prod_{\lambda, \alpha_\lambda} \mathcal{N}_{0\alpha_\lambda}(t)!,$$

where $\mathcal{N}_{0\alpha_\lambda}$ denotes the number of sample in the microstate m_{α_λ} in the λ -th component. In terms of $p_{\alpha_\lambda} = \mathcal{N}_{0\alpha_\lambda}(t)/\mathcal{N}_0$, this combination immediately leads to

$$S_0(t) \equiv \ln \mathcal{W}_0 / \mathcal{N}_0 = -\sum_\lambda \sum_{\alpha_\lambda} p_{\alpha_\lambda}(t) \ln p_{\alpha_\lambda}(t), \quad (25)$$

for the statistical entropy of the system and has already been used earlier¹⁹ by us; see Sec. 4.3.3 there. From what has been said above, this statistical entropy is also the thermodynamic entropy of a nonequilibrium state under component confinement for which the entropy is a state function of \mathbf{Z}_0 . Therefore, as before, we take \mathcal{S}_0 to be the general expression of the nonequilibrium thermodynamic entropy and use S_0 in place of \mathcal{S}_0 .

Introducing

$$p_\lambda(t) \equiv \sum_{\alpha_\lambda} p_{\alpha_\lambda}(t),$$

it is easy to see¹⁹ that

$$S_0(t) = \sum_\lambda p_\lambda(t) S_{0\lambda}(t) + S_C(t).$$

Here, the entropy of the component $\Gamma_{0\lambda}$ in terms of the reduced microstate probability $\hat{p}_{\alpha_\lambda} \equiv p_{\alpha_\lambda}/p_\lambda$ is

$$S_{0\lambda}(t) = -\sum_{\alpha_\lambda} \hat{p}_{\alpha_\lambda}(t) \ln \hat{p}_{\alpha_\lambda}(t) \quad (26)$$

so that the first contribution is its average over all components. The second term is given by

$$S_C(t) = -\sum_\lambda p_\lambda(t) \ln p_\lambda(t), \quad (27)$$

and represents the component entropy. It is this entropy that is related to the residual entropy³⁰ in disordered systems. The same calculation for a system in a medium will result in an identical formulation for the entropy as in Eq. (25) except that the sum is over components and microstates of the system.

IV. 1-DIMENSIONAL IDEAL GAS: A MODEL ENTROPY CALCULATION

We consider a gas of non-interacting identical structureless particles with no spin, each of mass m , confined to a 1-dimensional box of initial size $L = L_{\text{in}}$ with impenetrable walls (infinite potential well). Initially, the gas is in thermodynamic *equilibrium* with a medium at fixed temperature $T_{0\text{in}}$ and pressure $P_{0\text{in}}$. The gas is then isolated by disconnecting it from the medium. In time, the

isolated gas expands, may be in a nonequilibrium fashion. We wish to calculate its entropy as a function of the box size $L(t)$.

As there are no interactions between the particles, the wavefunction Ψ for the gas is a product of individual particle wavefunctions ψ . Thus, we can focus on a single particle to study the nonequilibrium behavior of the gas.^{34,35} The simple model of a particle in a box has been extensively studied in the literature but with a very different emphasis.^{36–38} The particle only has non-degenerate eigenstates whose energies are determined by $L = \alpha L_{\text{in}}$, $\alpha > 1$, and a quantum number k . We use the energy scale $\varepsilon_1 = \pi^2 \hbar^2 / 2m L_{\text{in}}^2$ to measure the energy of the eigenstate so that

$$\varepsilon_k(L) = k^2 / \alpha^2; \quad (28)$$

the corresponding eigenfunctions are given by

$$\psi_k(x) = \sqrt{2/L} \sin(k\pi x/L), \quad k = 1, 2, 3, \dots \quad (29)$$

The pressure generated by the eigenstate on the walls is given by⁶

$$P_k(L) \equiv -\partial \varepsilon_k / \partial L = 2\varepsilon_k(L)/L. \quad (30)$$

In terms of the eigenstate probability $p_k(t)$, the average energy and pressure are given by

$$\varepsilon(t, L) \equiv \sum_k p_k(t) \varepsilon_k(L), \quad (31a)$$

$$P(t, L) \equiv \sum_k p_k(t) P_k(L) = 2\varepsilon(t, L)/L. \quad (31b)$$

The entropy follows from Eq. (14) and is given for the single particle case by

$$s(t, L) \equiv -\sum_k p_k(t) \ln p_k(t).$$

The time dependence in $\varepsilon(t)$ or $P(t)$ is due to the time dependence in p_k and $\varepsilon_k(L)$. Even for an isolated system, for which ε remains constant, p_k cannot remain constant when the gas is not in equilibrium if L is held fixed after expansion. This follows directly from the second law¹⁹ and creates a conceptual problem because the eigenstates are mutually orthogonal and there can be no transitions among them to allow for a change in p_k .

A. Chemical Reaction Approach

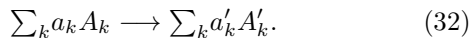
A way to change p_k in an isolated system is to require the presence of some stochastic interactions, whose presence allows for transitions among eigenstates.¹⁹ As these transitions are happening within the system, we can treat them as "chemical reactions" between different eigenstates^{27,39,40} by treating each eigenstate k as a chemical species. During the transition, these species undergoes chemical reactions to allow for the changes in their probabilities.

We follow this analogy further and extend the traditional approach^{27,39,40} to the present case. For the sake of

simplicity, our discussion will be limited to the ideal gas in a box; the extension to any general system is trivial. Therefore, we will use microstates instead of eigenstates in the following to keep the discussion general. Let there be $N_k(t)$ particles in the k th microstate at some instant t so that

$$N = \sum_k N_k(t)$$

at all times, and $p_k(t) = N_k(t)/N$. We will consider the general case that also includes the case in which final microstates refer to a box size L' different from its initial value L . Let us use A_k to denote the reactants (initial microstates) and A'_k to denote the products (final microstates). For the sake of simplicity of argument, we will assume that transitions between microstates is described by a single chemical reaction, which is expressed in stoichiometry form as



Let N_k and N'_k denote the population of A_k and A'_k , respectively, so that $N = \sum_k N_k = \sum_k N'_k$. Accordingly, $p_k(t) = N_k(t)/N$ for the reactant and $p_k(t + dt) = N'_k(t)/N$ for the product. The single reaction is described by a single extent of reaction ξ and we have

$$d\xi(t) \equiv -dN_k(t)/a_k(t) \equiv dN'_{k'}(t)/a'_{k'}(t) \quad \text{for all } k, k'.$$

It is easy to see that the coefficients satisfy an important relation

$$\sum_k a_k(t) = \sum_k a'_k(t),$$

which reflects the fact that the change $|dN|$ in the reactant microstates is the same as in the product microstates. The *affinity* in terms of the chemical potentials is given by

$$A(t) = \sum_k a_k(t) \mu_{A_k}(t) - \sum_k a'_k(t) \mu_{A'_k}(t),$$

and will vanish only in "equilibrium," i.e. only when p_k 's attain their equilibrium values. Otherwise, $A(t)$ will remain non-zero. It acts as the thermodynamic force in driving the chemical reaction.^{27,39,40} But we must wait long enough for the reaction to come to completion, which happens when $A(t)$ and $d\xi/dt$ both vanish. The extent of reaction ξ is an example of an internal variable. For the ideal gas under consideration, there does not seem to be any other internal variable as particles have no internal structures. In the following, we will assume only one internal variable $\xi(t)$.

B. Free (Sudden) Expansion of the Box

The box expands as a function of time, which need not be quasi-static (extremely slow) so there is no reason to assume that the gas remains in equilibrium after expansion. The entropy of the gas per particle can be

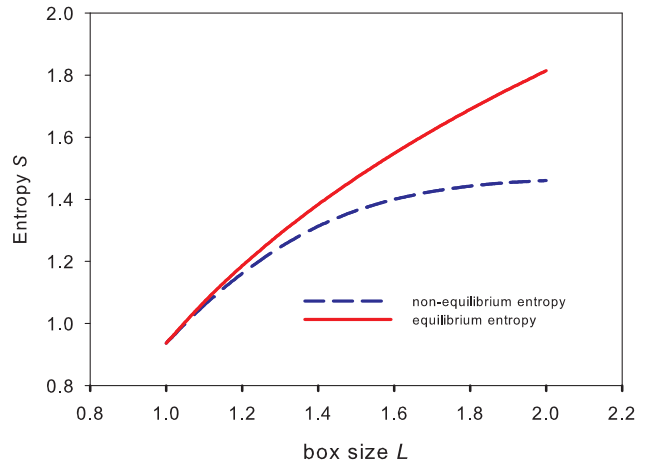


FIG. 2: The calculated equilibrium (continuous) and nonequilibrium (broken) entropies per particle for an ideal gas in a box as a function of the expansion box length L . The nonequilibrium state is the result of a sudden expansion from the initial state corresponding to $L = 1$ and $T_0 = 4$. The energy of the gas remains constant in the sudden expansion. As expected, the nonequilibrium entropy lies below the equilibrium entropy. In time, the former will increase to the latter as the gas equilibrates.

obtained by calculating $s(t, L) = -\sum_k p_k(t) \ln p_k(t)$ for the particle under consideration. Henceforth, we will call $s(t)$ the entropy of the particle, which shares the property that the irreversible entropy change $d_i s(t)$ will never be negative. All the above discussion about the chemical reaction is easily translated to the study of a particle in box without any change. The change $d_i p_n(t)$ is caused by the transitions between different eigenstates.

We consider the gas in *equilibrium* at some initial temperature T_{0in} in a box of length L_{in} , which we take to be $L_{in} = 1$. This is obtained by keeping the box in a medium of temperature T_{0in} . The corresponding microstate probabilities follow the Boltzmann law ($\beta_{in} \equiv 1/T_{0in}$):

$$p_{k,eq}(\beta_{in}, L_{in}) = \exp(-\beta_{in} \varepsilon_k(L_{in})) / Z_0(\beta_{in}, L_{in}),$$

where $Z_0(\beta_{in}, L_{in}) \equiv \sum_k \exp(-\beta_{in} \varepsilon_k(L_{in}))$ denotes the equilibrium partition function. The energy per particle in this gas is denoted by ε_{in} obtained by replacing $p_k(\beta, L)$ by $p_{k,eq}(\beta_0, L_{in})$ in Eq. (31); the corresponding pressure is $P_{0in} = 2\varepsilon_{in}/L_{in}$. The equilibrium entropy can be obtained by using $p_{k,eq}(\beta_0, L_{in})$ in S given in Eq. (20). The initial temperature T_{0in} for $L_{in} = 1$ is taken to be $T_{0in} = 4$ so that the initial energy $\varepsilon_{in} \approx 2.786$.

We now consider equilibrium states having the same initial thermodynamic energy ε_{in} for different values of L , even though the eigenstate energies and their Boltzmann probabilities vary with L . The corresponding equilibrium entropy $s_{eq}(t)$ as a function of L is shown in Fig. 2 by the continuous curve. Since the energy is constant, the

product $P_{0\text{eq}}(L)L = 2\varepsilon_{\text{in}}$ is also constant; see Eq. (31). Thus, $P_{0\text{eq}}(L)$ is a decreasing function of L . From the slope of the upper curve in Fig. 2 which decreases with L , we also conclude that $P_{0\text{eq}}(L)/T_{0\text{eq}}(L)$ is a decreasing function of L . Thus, $T_{0\text{eq}}(L)L$ is an increasing function of L . However, our calculation to be presented elsewhere³⁵ shows that $T_{0\text{eq}}(L)$ is also an increasing function of L . The eigenstates for a box of size L are given in Eq. (29).

We now consider nonequilibrium states. For this, we isolate the box from its medium and consider its free expansion as it expands suddenly from L_{in} to a new size $L > L_{\text{in}}$. Because of its isolation, its energy remains ε_{in} during this expansion. As the expansion is sudden, the initial eigenfunctions $\psi_{\text{lin}}(x)$ for L_{in} have no time to change, but are no longer the eigenfunctions of the new size L ; the latter are given by $\psi_k(x)$ in Eq. (29) for L . However, $\psi_{\text{lin}}(x)$ can be expanded in terms of $\psi_k(x)$ as a sum over k . We call this the quantum superposition principle. The corresponding expansion coefficients b_{kl} are easily seen to be³⁶

$$b_{kl}(L, L_{\text{in}}) = \frac{2l\alpha^{3/2}(-1)^l}{\pi(k^2 - \alpha^2 l^2)} \sin\left(\frac{k\pi}{\alpha}\right).$$

Using b_{kl} and $p_l(\beta_{\text{in}}, L, L_{\text{in}})$, we can determine the probability $p_k(\beta_{\text{in}}, L, L_{\text{in}})$ for the k th microstate in the new box, which allows us to determine all thermodynamic averages for the new box. We have checked that the new probabilities add to 1 and that the (average) energy after the free expansion is equal to ε_{in} to within our computational accuracy. Thus, $\Delta\varepsilon = 0$ in the sudden expansion. This is consistent with the fact that the gas does no external work and that no external heat is exchanged.

Despite this, the free expansion is spontaneous once the confining walls have moved. Therefore, the (thermodynamic) entropy of the gas must increase in this process in accordance with the second law. We use $p_k(\beta_{\text{in}}, L, L_{\text{in}})$ to evaluate the nonequilibrium statistical entropy, which is shown by the dashed curve in Fig. 2. The significance of this curve is as follows: Choose a particular value L in this graph. Then, the nonequilibrium entropy for this L is given by numerically evaluating the sum

$$s(\beta_{\text{in}}, L, L_{\text{in}}) = -\sum_k p_k(\beta_{\text{in}}, L, L_{\text{in}}) \ln p_k(\beta_{\text{in}}, L, L_{\text{in}}).$$

This is the entropy after the sudden expansion from the initial state at $L_{\text{in}} = 1$ and follows from the quantum superposition principle. Evidently, this entropy is higher than the initial equilibrium entropy $s_{\text{eq}}(\beta_{\text{in}}, L_{\text{in}})$. It is also obvious that this entropy has a memory of the initial state at $L_{\text{in}} = 1$ and $T_{0\text{in}} = 4$. Therefore, it does not represent the equilibrium entropy. If we now wait at the new value of L , the isolated gas in the new box will relax to approach its equilibrium state in which its nonequilibrium entropy will gradually increase until it becomes equal to its value on the upper curve.

V. 1-D TONKS GAS: A SIMPLE CONTINUUM MODEL

A careful reader would have realized by this time that the proposed entropy form in Eq. (14) is not at all the same as the standard classical formulation of entropy, such as for the ideal gas, which can be negative at low temperatures or at high pressures. The issue has been discussed elsewhere⁴¹ but with a very different perspective. Here, we visit the same issue from a very different perspective that allows us to investigate if and how the entropy in continuum models is related to the proposed entropy in this work. For this, we turn to a very simple continuum model in classical statistical mechanics: the Tonks gas,^{42,43} which is an athermal model and contains the ideal gas as a limiting case when the rod length l vanishes. We will simplify the discussion by considering the Tonks gas in one dimension. The gas consists of r impenetrable rods, each of length l lying along a line of length L . We will assume r to be fixed, but allow l and L to change with the state of the system, such as its pressure. The configurational entropy per rod determined by the configurational partition function is found to be⁴³

$$s_c = \ln[e(v - l)], \quad (33)$$

where v is the "volume" available per rod L/r . Even though the above result is derived for an equilibrium Tonks gas, it is easy to see that the same result also applies for the gas in internal equilibrium. The only difference is that the parameters in the model are also functions of internal variables now.

The entropy vanishes when $v = l + 1/e$ and becomes negative for all $v < l$. Indeed, it diverges to $-\infty$ in the incompressible limit $v = l$. This is contrary to the Boltzmann approach in which the entropy is determined by the number of microstates (cf. Eq. (1)) or the Gibbs approach (cf. Eq. (14)) and can never be negative. Can we reconcile the contradiction between the continuum entropy and the current statistical formulation?

We now demonstrate that the above entropy for the Tonks gas is derivable from the current statistical approach under some approximation, to be noted below, by first considering a lattice model for the Tonks gas and then taking its continuum limit. It is in the lattice model can we determine the number of microstates. In a continuum, this number is always *unbounded* (see below also). For this we consider a 1-d lattice Λ_f with N_f sites; the lattice spacing, the distance between two consecutive sites, is given by δ . We take $N_f \gg 1$ so that $L_f = (N_f - 1)\delta \approx N_f\delta$ is the length of the lattice Λ_f . We randomly select r sites out of N_f . The number of ways, which then represents the number of configurational microstates, is given by

$$W_c = N_f! / r!(N_f - r)! \quad (34)$$

After the choice is made, we replace each selected site by $\lambda + 1$ consecutive sites, each site representing an atom

in a rod, to give rise to a rod of length $l \equiv \lambda\delta$. It is clear that δ also changes with the state of the system. The number of sites in the resulting lattice Λ is

$$N = N_f + r\lambda$$

so that the length of Δ is given by $L = (N - 1)\delta \approx N\delta$ since $N \gg 1$. We introduce the number densities $\varphi_f = r/N_f$, $\rho_f = r/N_f\delta \approx r/L_f$ and $\rho = r/N\delta \approx r/L$. A simple calculation shows that $S = \ln W_c$ is given by

$$S = -N_f[\rho_f \delta \ln \rho_f \delta + \ln(1 - \rho_f \delta) - \rho_f \delta \ln(1 - \rho_f \delta)].$$

This result can also be obtained by taking the athermal entropy for a polydisperse polymer solution a Bethe lattice⁴⁴ by setting the coordination number q to be $q = 2$. We now take the continuum limit $\delta \rightarrow 0$ for *fixed* ρ_f and ρ , that is *fixed* L_f and ρL , respectively. In this limit, $\ln(1 - \rho_f \delta) \approx -\rho_f \delta$, and $\rho_f \delta \ln(1 - \rho_f \delta) \approx -(\rho_f \delta)^2$. Use of these limits in S yields

$$S = -r \ln(e/\rho_f \delta) \rightarrow \infty. \quad (35)$$

The continuum limit of the entropy from the Boltzmann approach has resulted in a diverging entropy regardless of the value of ρ_f ,⁴¹ a well known result. By introducing an arbitrary *constant* a with the dimension of length, we can rewrite S as

$$S/r = -\ln(e/\rho_f a) + \ln(\delta/a), \quad (36)$$

in which the first term remains finite in the continuum limit, and the second term contains the divergence. The diverging part, although explicitly independent of ρ_f , still depends on the state of the gas through δ , and cannot be treated as a constant unless we assume δ to be independent of the state of the gas. It is a common practice to approximate the lattice spacing δ as a constant. In that case, the diverging term represents a constant that can be subtracted from S/r . Recognizing that $1/\rho_f = v - l$, we see that the first term in Eq. (36) is nothing but the entropy of the Tonks gas in Eq. (33) for the arbitrary constant $a = 1$. However, this equivalence only occurs in the state independent constant- δ approximation.

As the second term above has been discarded, the continuum entropy s_c also has *no* simple relationship with the number (≥ 1) of microstates in the continuum limit, which means that the continuum entropy cannot be identified as the Boltzmann entropy in Eq. (17). To see this more clearly, let us focus on the centers of mass of each rod, which represent one of the r sites that were selected in Λ_f . Each of the k sites x_k , $k = 1, 2, \dots, r$, is free to move over L_f . The *adimensional* volume $|\Gamma_f|$, also called the probability and denoted by Z by Boltzmann,^{17,23} of the corresponding phase space Γ_f is L_f^r/a^r . However, contrary to the conventional wisdom,²³ $\ln |\Gamma_f|$ does not yield s_c . The correct expression is given by the Gibbs-modified adimensional volume $|\Gamma_f|/r!$, i.e.

$$\frac{1}{r!a^r} L_f^r.$$

The presence of $r!$ is required to restrict the volume due to indistinguishability of the rods à la Gibbs. For large r , this quantity correctly gives the entropy s_c . However, this quantity is not only not an integer, it also cannot be *always* larger than or equal to unity, as noted above.

VI. SEMI-CLASSICAL APPROXIMATION IN PHASE SPACE FOR S

The analog of a quantum microstate in classical statistical mechanics is normally obtained by recognizing that in the *adiabatic approximation*, each small phase space cell of volume element $dx_c (= dpdq$ in terms of generalized coordinates q and momenta p) of size h^s corresponds to a microstate,^{4,5} where s is the degrees of freedom of the system. The latter follows from the Bohr-Sommerfeld quantization rule for a periodic motion. The adiabatic approximation requires the parameters characterizing the system to vary extremely slowly. We will assume one such parameter λ (such as the volume V) so that⁴⁵ $\tau\lambda \ll \lambda$, where τ is the period of oscillation for constant λ ; the system would be isolated in the latter case. In the above approximation, the energy of the system will vary very slowly and can be taken to be constant over a period of oscillation. The action taken over the closed path for the constant value of λ and the energy is quantized⁶:

$$I = \oint pdq = (n + 1/2)h.$$

This observation is the justification of the above cell size of a classical microstate. Thus, the number of "classical" microstates is given by

$$W = \Delta\Gamma/h^s,$$

where $\Delta\Gamma$ is the phase space volume corresponding to the system. This allows us to divide the phase space into W cells, index by k , of volume $dx_k = dx_c$ and "centered" at x_k at some time which we call the initial time $t = 0$. We will denote the evolution of the cell at time t by the location of its "center" $x_k(t)$ and its volume element $dx_k(t)$. In terms of the distribution function $f(x, t)$ in the phase space, the k th microstate probability therefore is given by

$$p_k(t) \equiv f(x_k, t)dx_k(t). \quad (37)$$

Evidently,

$$\sum_k f(x_k, t)dx_k(t) = 1 \quad (38)$$

at all times. The entropy and the average of any observable $O(x, t)$ of the system are given by

$$S(t) \equiv -\sum_k f(x_k, t)dx_k(t) \ln[f(x_k, t)dx_k(t)], \quad (39a)$$

$$\overline{O}(t) \equiv \sum_k O(x_k, t)f(x_k, t)dx_k(t), \quad (39b)$$

the sum being over all W microstates. While it is easy to see that continuum analogs for Eqs. (38) and (39b)

are easily identified, this is not so for the entropy in Eq. (39a).⁴⁶ However, it should be obvious that S_f in Eq. (3) cannot be a candidate for the statistical entropy $S(t)$.

It is well known⁶ that the system in the adiabatic limit remains in the same quantum state. For Hamiltonian dynamics, the conservation of the phase space cell volume under evolution ensures $dx_k = dx_c$ for each cell so that $\dot{x} = 0$. This results in the incompressibility of the phase space. In equilibrium, $f(x_k, t)$ is not only uniform but also constant, and we conclude from Eq. (38) that this value is $f = 1/\Delta\Gamma$. Accordingly, $p_k = 1/W$ in equilibrium as expected and we obtain the equilibrium entropy $S_{\text{eq}} = \ln W$.

The situation is far from clear for nonequilibrium states. As the example of expansion of the box shows, the system is no longer restricted to be in the same microstate, which means that the microstate energy is no longer a constant and the phase space trajectory is no longer closed. Thus, the suitability of the Bohr-Sommerfeld quantization is questionable, and care must be exercised to identify the microstates. We will adopt the following prescription. We consider some equilibrium state (uniform $f(x)$) of the isolated system to identify the cell volume $dx_c = h^s$. Once the identification has been done, we will no longer worry about its relationship with h^s , and only deal with the cells. We then follow the evolution of each cell in time in a nonequilibrium process during which $\dot{x} = 0$ may not hold. Thus the volume of each cell may no longer be constant. The process may also result in changes in $f(x_k, t)$.⁴⁷ Indeed, it is quite possible that f diverges at the same time that dx_c vanishes.⁴⁸ However, their product, which determines the microstate probability, must remain strictly bounded and ≤ 1 . In particular, as the cell volume shrinks to zero, f must diverge to keep the product bounded. Thus, the divergence^{49,50} of f alone does not imply that the entropy diverges to negative infinity.

This is easily seen by the following 1-d damped oscillator, the standard prototype of a dissipative system:⁴⁵ $\ddot{x} + 2\kappa\dot{x} + \omega_0^2 x = 0$ with a (positive) damping coefficient, which is chosen such that $\kappa > \omega_0$ just for simplicity. We have the case of aperiodic damping. We will only consider the long time behavior. It is easy to see that in this limit ($\kappa' = \kappa + \sqrt{\kappa^2 - \omega_0^2}$)

$$dx_c \sim \exp(-2\kappa't), \quad f \sim \exp(+2\kappa't),$$

and their product remains bounded, as expected.

VII. JAYNES REVISITED

Boltzmann¹⁵ provides the following alternative expression of the entropy^{15,51} in terms of a single particle probability $p_i^{(1)}$ for the particle to be in the i th state:

$$S_B^{(1)} = -N \sum_i p_i^{(1)} \ln p_i^{(1)}, \quad (40)$$

not to be confused with that in Eq. (1). Boltzmann is only interested in the maximum entropy, which occurs

when all states are equally probable. In this case,

$$S_{B, \text{max}}^{(1)} = N \ln w$$

where w is the number of possible states of a single particle in the gas. In general, particles are not independent due to interactions and number of possible states $W < w^N$. Accordingly, maximum Gibbs entropy S_{max} per particle is *less* than the corresponding equiprobable Boltzmann entropy $S_{B, \text{max}}^{(1)}$. However, Jaynes¹⁸ gives a much stronger results, see his Eq. (5):

$$S < S_B^{(1)}.$$

The equality occurs only if there are no interactions between the particles, as we have asserted above.

VIII. SUMMARY AND DISCUSSION

Recognizing that there does not exist a first principles statistical formulation of nonequilibrium thermodynamic entropy for an isolated system in terms of microstate probabilities, we have attempted to fill in the gap. We use a formal approach (frequentist interpretation of probability) by extending the equilibrium ensemble of Gibbs to a nonequilibrium ensemble, which is nothing but a large number \mathcal{N}_0 of samples of the thermodynamic system under consideration. Accordingly, we refer to the ensemble as a sample space. The formal approach enables us to evaluate the combinatorics for a given set of microstate probabilities. The resulting statistical entropy is independent of the number of samples and depends only on the probabilities as is seen from Eqs. (14) and (25). Thus, the use of a large number of samples is merely a formality and is not required in practice. We have shown that in equilibrium, the statistical entropy is the same as the equilibrium thermodynamic entropy: $S_0(\mathbf{X}_0) = S_0(\mathbf{X}_0)$. But we have also shown that the statistical entropy is equal to the nonequilibrium thermodynamic entropy, provided the latter is a state function of the nonequilibrium state variables $\mathbf{Z}_0(t)$: $S_0(\mathbf{Z}_0(t)) = S_0(\mathbf{Z}_0(t))$. We cannot make any comment about the relationship between $S_0(\mathbf{Z}_0(t), t)$ and $S_0(\mathbf{Z}_0(t), t)$ for the simple reason that there is no way to measure or calculate a non-state function $S_0(\mathbf{Z}_0(t), t)$. We should remark here that the standard approach to calculate nonequilibrium entropy is to use the classical nonequilibrium thermodynamics²⁷ or its variant, which treats the entropy at the local level as a state function.

Some readers may think that our statistical formulation is no different than that used in the information theory. We disagree. For one, there is no concept of internal variables ξ_0 in the latter theory. Because of this, our approach allows us to consider three levels of description so that we can consider three different entropies $S(\mathbf{Z}_0(t), t)$, $S_0(\mathbf{Z}_0(t))$ and $S_0(\mathbf{X}_0)$ satisfying the inequalities in Eq. (18). The information theory can only deal

with two levels of entropies. There is also no possibility of a residual entropy in the latter.

For an isolated system in internal equilibrium ($p_\alpha = p$ for $\forall m_\alpha$), just a single sample will suffice to determine the entropy as samples are *unbiased*. The entropy in this case is no different than the "entropy" $-\ln p$ of a single sample:^{19,23}

$$S(t) = (-p \ln p) W_0 = -\ln p = \ln W_0,$$

where W_0 represents $W_0(\mathbf{Z}_0(t))$ or $W_0(\mathbf{X}_0)$. However, this simplicity is lost as soon as the system is not in internal equilibrium. Here, one must consider averaging over all microstates.

Changes in microstate probabilities result in changes in the entropy. There are two ways probabilities can change within an isolated system, both of them being irreversible in nature. One cause of changes is due to the quantum nature as seen in the sudden expansion of the box. Here, the parameter λ ($= L$) changes non-adiabatically and creates irreversibility. The resulting irreversible change

in the entropy for the 1- d gas has been calculated and shown by the lower curve in Fig. 2. The other cause of probability changes is due to the "chemical reaction" going on among the microstates that brings about equilibration in the system. The corresponding irreversible rise in the entropy for the gas is shown by the difference between the two curves in Fig. 2. The interaction of a body with its medium can also result in the changes in microstate probabilities, and has been considered elsewhere.⁵²

We consider the continuum analog of the statistical formulation of entropy and show that the standard formulation, S_f in Eq. (3), is not a good candidate of the nonequilibrium entropy. It is then argued that the divergence of f in some cases, see the discussion above, makes S_f diverge to $-\infty$, even though the statistical entropy remains finite and positive. Thus, S_f cannot be equated with our statistical formulation, a generalization of the Gibbs formulation. We suggest that our statistical Gibbs formulation can be applied to any nonequilibrium state.

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